Single Crystal Growth and Characterization of Yb3+doped Rare Earth Orthoaluminates for Scintillator Application(シンチレータ用Yb3+添加希土類オルソアルミネート単結晶の成長と評価)

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論文内容要旨

Chapter 1. Introduction

In recent years, strong effort has been made to identify and develop scintillator materials characterized by high light output, fast response and high density, thus specific composition required for future medical imaging applications. BaF_2 single crystal is a fast scintillator commonly used as material for time-of-flight (TOF) - positron emission tomography (PET) detectors. However, BaF_2 single crystal has the disadvantage of low density (4.88 g/cm^3) and an additional slow decay time (620 ns). Thus, the focus of this study is to investigate and search for Yb^{3+}-doped rare-earth orthoaluminate single crystals, which are suitable as super-fast scintillator host material and exhibiting superior scintillation properties compared with BaF_2 single crystal.

In this study a new scintillator crystal, Yb^{3+}-doped $YAlO_3$ was grown by the micro-pulling-down and Czochralski methods. $YAlO_3$ crystals fulfill properties like high hardness, non-hygroscopicity, mechanical and chemical stability and good optical properties. The purpose of this study is to reveal the conditions of twin and inclusion-free Yb^{3+}-doped $YAlO_3$ single crystals. Due to the fast charge transfer (CT) luminescence of Yb^{3+} in near UV-visible spectral range and higher density of Yb-rich $YAlO_3$, such material is promising candidate for very fast scintillators. Furthermore, Yb^{3+}-doped $(Lu,Y)AlO_3$ perovskite-type single crystals were investigated. The crystals to be used for tomographs must possess high density and high atomic number for efficient gamma ray detection. The $YAlO_3$ has lower density (5.36 g/cm^3) compared to $LuAlO_3$ (8.34 g/cm^3). For the higher density, lutetium was introduced to $YAlO_3$ as Yb^{3+}-doped $(Lu,Y)AlO_3$ crystal.

The main purposes of this thesis are: (1) to search for super-fast scintillator (decay time with less than 1 ns) material with perovskite structure using Yb^{3+}-CT luminescence and (2) to find a material containing higher density compared to BaF_2 and no slow components in the decay time for application in TOF-PET

medical imaging system.

Chapter 2. Experimental

This chapter describes experimental procedures used for the material synthesis, growth and characterization for Yb^{3+}-doped rare-earth orthoaluminate single crystals. The high purity Y_2O_3, Lu_2O_3, α-Al_2O_3 and Yb_2O_3 powders, 4N and above, were used as the starting materials in the synthesis of perovskite group materials. The mixed materials were prepared by a traditional solid state reaction from stoichiometric amounts of powders at 1650 °C for 96 hours and at 1750 °C for 72 hours. The X-ray diffraction (XRD) patterns of powders were measured for examining phase identification using a diffractometer with $CuK_{\alpha 1}$ radiation. Before the Czochralski growth, the micro-pulling-down (μ-PD) method was applied in order to investigate the features of the grown crystals and to verify whether melt growth of new compositions is possible. For the growth of bulk and high-quality single crystals, the Czochralski (Cz) method was applied.

Quantitative analysis of elements along the pulled crystal and perpendicular to the growth direction was performed by the electron probe microanalysis (EPMA). The structure analysis of the grown single crystals was performed by single crystal XRD. The crystallinity was characterized by X-ray rocking curve (XRC) analysis for the (200) reflection of grown Yb^{3+}-doped $YAlO_3$ crystal using a high-resolution diffractometer with $CuK_{\alpha 1}$ radiation diffracted by a four-crystal Ge (220) channel monochromator. Absorption measurements were performed at room temperature (RT) with the Shimadzu 3101 PC UV-VIS-NIR spectrometer. Photoluminescence (PL) and radioluminescence (RL) spectra and decays were measured with a modified Spectrofluorometer 199S using excitation with a steady-state or ns pulsed hydrogen discharge flashlamps, X-ray tube and ^{22}Na radioisotope, respectively. Wavelength-resolved thermally stimulated luminescence (TSL) measurements were performed in the 10 - 310 K range after X-ray irradiation at 10 K, with a home made apparatus allowing the detection of the TSL signal both as a function of temperature and wavelength.

Chapter 3. Growth of $REAlO_3$ single crystals with RE=Y, Yb, Lu

In this chapter, the solid solution range of $(Y_{1-x}Yb_x)AlO_3$ and $(Lu_xY_{0.9-x}Yb_{0.1})AlO_3$ was studied by phase identification of sintered samples using powder XRD. From the XRD pattern of different $(Y_{1-x}Yb_x)AlO_3$ powders, it is concluded that the single phase region of the perovskite-type $(Y_{1-x}Yb_x)AlO_3$ solid solution is within $0.0 \leq x < 0.5$. From the XRD pattern of different $(Lu_xY_{0.9-x}Yb_{0.1})AlO_3$ powders, it is concluded that the single phase region of the perovskite-type $(Lu_xY_{0.9-x}Yb_{0.1})AlO_3$ solid solution is within $0.0 \leq x < 0.45$.

Based on the consideration of single phase region for $(Y_{1-x}Yb_x)AlO_3$ and $(Lu_xY_{0.9-x}Yb_{0.1})AlO_3$, $(Y_{1-x}Yb_x)AlO_3$ and $(Lu_xY_{0.9-x}Yb_{0.1})AlO_3$ single crystals have been successfully grown by the μ-PD and Cz methods with the radio frequency system. The best $(Y_{1-x}Yb_x)AlO_3$ and $(Lu_xY_{0.9-x}Yb_{0.1})AlO_3$ single crystals were obtained for a growth rate equal to 0.12 mm/min in the μ-PD and 1.0 mm/h in the Cz method. Derived from the investigation on the morphological study of $(Y_{1-x}Yb_x)AlO_3$ crystal, the high ytterbium concentration tends to cause a relative instability of the perovskite phase during the crystal growth.

Chapter 4. Homogeneity and crystallographic structure

The present chapter reports the results of the homogeneity and the crystallographic structure in the single crystals of Yb^{3+}-doped rare-earth orthoaluminate. The center of crystals (solidification fraction g, g = 0.5) grown by Cz method was selected for all analysis.

$(Y_{1-x}Yb_x)AlO_3$ and $(Lu_xY_{0.9-x}Yb_{0.1})AlO_3$ crystals have a good compositional homogeneity both perpendicular and parallel to the growth axis. The distribution coefficients of Yb^{3+} in $YAlO_3$ and $(Lu,Y)AlO_3$ were close to unity. As the Yb concentration increase, the R-O average interatomic distance (2.392 Å) for $(Y_{0.7}Yb_{0.3})AlO_3$ becomes shorter than R-O distance (2.402 Å) for $(Y_{0.9}Yb_{0.1})AlO_3$. Whereas, the Al-O average interatomic distance (1.910 Å) for $(Y_{0.7}Yb_{0.3})AlO_3$ is similar to Al-O distance (1.911 Å) for $(Y_{0.9}Yb_{0.1})AlO_3$. The R atoms are coordinated to eight oxygen atoms at average distance 2.396 Å for $(Lu_{0.1}Y_{0.8}Yb_{0.1})AlO_3$ and 2.391 Å for $(Lu_{0.3}Y_{0.6}Yb_{0.1})AlO_3$. Compared with the R-O distance in $(Lu_{0.3}Y_{0.6}Yb_{0.1})AlO_3$, in $(Lu_{0.1}Y_{0.8}Yb_{0.1})AlO_3$ the R-O distance is slightly longer. Whereas, the Al-O average interatomic distance (1.910 Å) for $(Lu_{0.1}Y_{0.8}Yb_{0.1})AlO_3$ was similar to Al-O distance (1.909 Å) for $(Lu_{0.3}Y_{0.6}Yb_{0.1})AlO_3$. These results support that the higher Yb and Lu concentrations contributing to the formation of a more distorted perovskite lattice. By XRC analysis, the crystallinity of $YAlO_3$:Yb crystal is almost perfect and the structure is of high quality. $YAlO_3$:Yb crystals with a lower ytterbium concentration shows a higher structural quality.

Chapter 5. Luminescence and scintillation properties

The CT luminescence of Yb^{3+} in $YAlO_3$ and $(Lu,Y)AlO_3$ is treated in this chapter. The absorption, scintillation, PL and thermoluminescence characteristics of Cz grown $(Y_{1-x}Yb_x)AlO_3$ and $(Lu_xY_{0.9-x}Yb_{0.1})AlO_3$ single crystals are described.

The CT luminescence is observed in a perovskite host lattices. The CT emission bands are broad and the Stokes shifts are large (about 10 000 cm^{-1}). Luminescence spectra are dominated by the CT luminescence of Yb^{3+}, peaking at about 345 nm and 525 nm. Under X-ray excitation, the intensity of Yb^{3+}-CT luminescence is increasing with x and reaches at RT more than 11 % of $Bi_4Ge_3O_{12}$ for x = 0.45 in $(Y_{1-x}Yb_x)AlO_3$, while at 80 K it is over 170 % of $Bi_4Ge_3O_{12}$ for $x \geq 0.3$. In Fig. 1, scintillation decay shows a dominant decay time of 0.87 ns for $(Y_{0.55}Yb_{0.45})AlO_3$ and no significant slow components were detected. The PL decay time can be tuned by temperature and Yb concentration from some tens of nanoseconds at 80 K down to about 0.8 ns at 295 K. Due to thermal quenching, the decay time is shortened to subnanosecond values and becomes

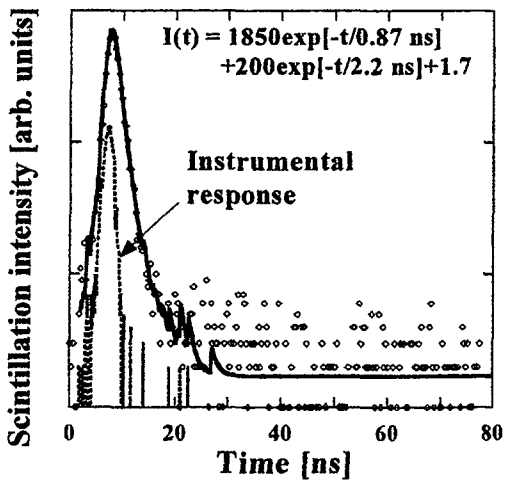

Fig. 1. Scintillation decay of $(Y_{0.55}Yb_{0.45})AlO_3$ at RT.

comparable with the cross-luminescence decay time in BaF_2. The thermoluminescence glow curve of Yb^{3+}-doped $YAlO_3$ reveals a very low concentration of shallow traps compared to the Zr^{4+} co-doped $YAlO_3$:Ce scintillator (Fig. 2). Absorption, RL and luminescence decay kinetics of Yb^{3+}-doped $(Lu,Y)AlO_3$ were found to be similar to those of Lu-free Yb^{3+}-doped $YAlO_3$. The decay time of Yb^{3+}-doped $(Lu,Y)AlO_3$ (0.92 ns) is about 20 times faster than Ce^{3+}-doped $(Lu,Y)AlO_3$. The decay time is not dependent on Lu concentration and only depends on the Yb concentration.

The Yb-rich concentration in $(Y_{1-x}Yb_x)AlO_3$ shows fastest decay times and makes this material a promising candidate for "*super-fast scintillators*" as TOF-PET application.

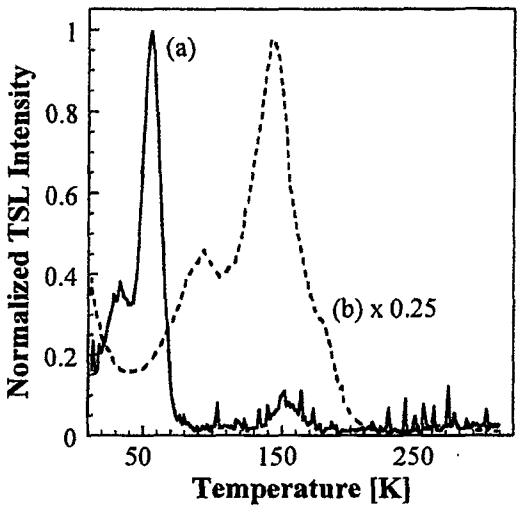

Fig. 2. TSL glow curve after X-ray irradiation of the $(Y_{0.7}Yb_{0.3})AlO_3$ sample (curve (a)) and of $YAlO_3$. 1 % Ce, 1000 ppm Zr (curve (b)).

Chapter 6. Conclusion

This study investigates the CT luminescence of Yb^{3+} in $YAlO_3$ and $(Lu,Y)AlO_3$ perovskites as new super-fast scintillator materials. To obtain higher density, lutetium was introduced to Yb^{3+}-doped $YAlO_3$ crystal. Yb^{3+}-doped $YAlO_3$ and $(Lu,Y)AlO_3$ single crystals have been successfully grown by the μ-PD and Cz methods. Material synthesis, growth, homogeneity and structural characterization of the crystals are investigated. The luminescence and scintillation properties of Yb^{3+}-doped $YAlO_3$ and $(Lu,Y)AlO_3$ single crystals are discussed.

Very fast CT luminescence of Yb^{3+} from the near ultraviolet to the visible spectral range makes Yb-rich $YAlO_3$ a promising candidate for "*super-fast scintillators*" comparable to BaF_2 single crystal. Super-fast decay time (0.75 ns) and no slow decay components make $YAlO_3$:Yb(45 %) single crystal very attractive for TOF-PET medical imaging system.

論文審査結果の要旨

近年、医療現場において医療画像技術であるポジトロン断層法（PET）が注目されている。これは癌やアルツハイマーといった難病の部位の特定に用いられる技術であり、医療現場からはその分解能向上が求められている。

分解能を向上させるには、材料であるシンチレータの応答速度の向上が重要な鍵を握る。PETの分解能を向上させ、より的確な患部の特定を可能にするためにはTime of Flight（TOF）型のPETを用いることが有効である。しかしながら、このTOF-PETは、これまでBaF_2などの短寿命シンチレータも用いることにより実用化が試みられてきたが、密度が低い、発光量が少ない、長寿命成分が存在する、発光波長が300nm以下であり特殊な光電子増倍管を用いねばならないなどの理由から実現しなかった経緯がある。本研究は、BaF_2とは別の発光メカニズムであるYbのチャージトランスファ状態からの発光を用いてTOF-PET用の短寿命シンチレータ材料の開発に取り組んだ経過をまとめたもので、全6章からなる。

第1章は、序論であり、本研究の背景と目的を述べている。

第2章では、実験方法を述べている。研究対象のYb^{3+}添加希土類オルソアルミネートを研究する際、まず、固相反応により固溶体の組成比を変えたものを全比率で準備し、それを粉末X線回折法により相を同定することで固溶域を調べ、マイクロ引下げ法や引上げ法といった手法で結晶成長を行った。各種イオンの組成分布は電子線マイクロプローブ分析装置（EPMA）にて測定した。構成元素の結晶構造中で占めるサイトは単結晶X線構造解析法により追跡した。紫外から可視域による吸収、紫外線励起による発光の測定に加え、X線励起およびγ線励起によるシンチレーション特性を行った。また、点欠陥のマクロな評価として熱蛍光測定も行った。

第3章では、研究対象であるYb^{3+}添加希土類オルソアルミネート単結晶の成長を可能にしている。結晶成長方法は、材料探索の観点から高速の結晶作製方法としてマイクロ引下げ法を、物性測定を厳密に行うため高品質単結晶を作製する観点から引上げ法をそれぞれ選択し、その結晶成長方向の温度勾配を適切に設定するなどすることでYb^{3+}添加希土類オルソアルミネート単結晶の成長方法を確立した。

第4章では、作製した結晶の組成の均質性を調べている。また、単結晶X線構造解析法により、構成元素が結晶構造中で占めるサイトの特定を行い、構成元素が目的のサイトを占めていることを確かめた。また、X線ロッキングカーブの測定から、本研究で作製した結晶が市販の光学結晶と同等の結晶性を有していることを確かめた。

第5章では、シンチレーション特性に関連する光学特性評価を行った。紫外から可視域による吸収によりYbの電荷移動状態（CTS）の吸収の有無を確認し、紫外線によりYbのCTSを直接励起することでCTSからの発光を測定した。結晶をシンチレータとして使用する場合、エネルギーを母結晶で吸収した場合も同様の発光が（短寿命で）起こる必要がある。そこで、本章ではシンチレーション特性評価として、X線励起およびγ線励起においても、CTSからの発光があることを確認した。Ybを30%置換させたYAP結晶の発光量は既存のTOF-PET用シンチレータであるBaF_2をやや下回るものであったが、室温における蛍光寿命はBaF_2の8割程度と短い値を示した。発光波長もBaF_2に比して100nm程度長波長であるため特殊な光電子増倍管を用いる必要がなく、加えて、密度はBaF_2を上回り、且つ、長寿命成分もないなど優れた特性を示した。また、熱蛍光測定により、蛍光寿命を長くしてしまう原因となる点欠陥濃度が、市販のシンチレータ結晶であるCe:YAPと比較して一桁以上少ないことを明らかにした。

第6章は、総括であり、本研究で得られた成果を要約している。

以上、要するに本論文は、TOF-PET用シンチレータに資する短寿命シンチレータの開発を目的とし、結晶性および均一性に優れたYb^{3+}添加希土類オルソアルミネート結晶の融液からの単結晶成長方法の確立と、希土類オルソアルミネートを母結晶とした場合のYbの電荷移動状態からの発光機構を明らかにしたもので、材料工学の発展に寄与するところが少なくない。

よって、本論文は博士(工学)の学位論文として合格と認める。